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# PATENT COOPERATION TREATY

WO 01/12437  
PCT/JP00/03904

PCT

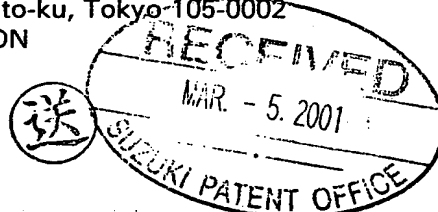
## NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

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6-7, Atago 1-chome  
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JAPON



|   |   |                  |
|---|---|------------------|
| Date of mailing (day/month/year)<br>22 February 2001 (22.02.01) |   |                  |
| Applicant's or agent's file reference<br>/ 219MD/PCT            |   | IMPORTANT NOTICE |
| International application No.<br>PCT/JP00/03904                 | International filing date (day/month/year)<br>15 June 2000 (15.06.00) |                  |
| Priority date (day/month/year)<br>18 August 1999 (18.08.99)     |   |                  |
| Applicant<br>DU PONT-MITSUI POLYCHEMICALS CO., LTD. et al       |   |                  |

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:  
KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:  
CN,EP

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 22 February 2001 (22.02.01) under No. WO 01/12437

### REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

### REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

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# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

|   |   |  |
|---|---|--|
| Applicant's or agent's file reference<br><b>1219MD/PCT</b>            | <b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below. |  |
| International application No.<br><b>PCT/JP 00/ 03904</b>              | International filing date (day/month/year)<br><b>15/06/2000</b>   | (Earliest) Priority Date (day/month/year)<br><b>18/08/1999</b> |
| Applicant<br><br><b>DU PONT-MITSUI POLYCHEMICALS CO., LTD. et al.</b> |   |  |

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

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(54) Title: LAMINATED FILM AND METHOD OF PRODUCING THE SAME

(57) Abstract: A laminated film exhibiting excellent interlayer adhesiveness obtained by extrusion-laminating a resin directly on a polyester film without effecting anchor-coating or without treating the molten film of the extrusion-laminated resin with ozone. The laminated film is obtained by extrusion-laminating, onto the polyester film, an ethylene copolymer containing an unsaturated carboxylic acid and a (meth)acrylic acid ester, which may be further blended with a small amount of an ethylene/ $\alpha$ -olefin copolymer having a density of 840 to 900 kg/m<sup>3</sup>, the amount of the unsaturated carboxylic acid component being from 1 to 12 % by weight and the amount of the (meth)acrylic acid ester component being from 2 to 25 % by weight.



**WO 01/12437 A1**

## DESCRIPTION

LAMINATED FILM AND METHOD OF PRODUCING THE SAME  
(Technical Field)

5       The present invention relates to a polyester  
laminated film obtained by extrusion-laminating an  
ethylene copolymer resin onto a polyester film, exhibiting  
excellent interlayer adhesiveness to the polyester  
surface, and to a method of producing the same. More  
10 specifically, the invention relates to a method of  
producing a polyester laminated film having excellent  
interlayer adhesiveness by the extrusion-lamination  
without effecting the anchor-coat treatment on the  
polyester film or without effecting the ozone treatment on  
15 the laminated resin film, and to a laminated film obtained  
by the above method.

(Background Art)

A polyester film and, particularly, a biaxially  
stretched polyester film exhibits excellent transparency,  
20 toughness and oxygen barrier property, and has been widely  
used as a base member of packaging materials for packaging  
foods and industrial materials. In practice, other base  
member that plays the roll of a reinforcing member, such  
as polyamide film, ethylene/vinyl alcohol copolymer,  
25 aluminum foil, aluminum-deposited polyester film,  
inorganic material-deposited polyester film or paper, is  
further laminated on the polyester film and, besides, a  
heat-sealing resin layer is laminated thereon to impart  
heat-sealing property.

30       The films can be laminated by such a laminating  
method as dry-laminating method, wet-laminating method or  
extrusion-laminating method. Among them, the extrusion-  
laminating method is widely used which is most  
advantageous from the standpoint of cost of production and  
35 efficiency. Here, the lamination of the polyester film on

the other base member, or the lamination of a heat-sealing layer on the polyester film, is executed by a method which extrusion-laminates an adhesive resin between the polyester film and the other member for the former case or  
5 is executed by a method which extrusion-laminates a heat-sealing resin on the polyester film for the latter case.

Here, in order to reinforce the interlayer adhesion between the polyester film and the laminated resin, there is generally employed either (1) a method of effecting the  
10 extrusion-lamination after the anchor-coating agent has been applied onto the surface of the polyester film, or (2) a method of executing the ozone treatment on the surface of the molten resin film on where the extrusion laminate is to be adhered as well as the corona treatment  
15 and flame treatment on the surface of the polyester film at the time of executing the extrusion lamination. Otherwise, so high interlayer adhesion is not obtained.

However, the above-mentioned method (1) involves such problems as deteriorated working environment due to the  
20 scattering of a diluting organic solvent such as ethyl acetate or toluene used as the anchor-coating agent at the time of extrusion-lamination, a rise in the cost of production due to the use of a relatively expensive anchor-coating agent and offensive odor due to organic  
25 solvent remaining in the final product (packaging material). On the other hand, the above-mentioned method (2) involves such problems that expensive ozone-treating apparatus and surface-oxidizing apparatus must be provided in a process in the extrusion-laminate processing,  
30 requiring extra investment for the facilities and driving up the cost of operation.

It has therefore been strongly urged in the field of packaging industries to provide a method of producing a polyester laminated film having favorable interlayer  
35 adhesiveness by the extrusion-laminating method without

using the anchor-coating agent or the ozone-treating apparatus which has been so far considered essential. In order to satisfy the above requirement, therefore, the present inventors have conducted keen study, have

- 5 discovered the fact that use of the anchor-coating agent and the ozone-treating apparatus can be omitted when a resin having a particular composition is extrusion-laminated on the polyester film, and have arrived at the present invention.

10 (Summary of the Invention)

It is therefore an object of the present invention to provide a method of producing a laminated film having excellent interlayer adhesiveness based on the extrusion-lamination method by laminating the polyester films or by  
15 laminating the polyester film on another base member film, and a laminated film obtained by this method.

That is, the present invention is concerned with a laminated film obtained by extrusion-laminating, onto at least one surface of a polyester film, an  
20 ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer or a mixture resin composition thereof with an ethylene/unsaturated carboxylic acid copolymer and/or an ethylene/(meth)acrylic acid ester copolymer, the amount of the unsaturated carboxylic acid component being  
25 from 1 to 12% by weight and the amount of the (meth)acrylic acid ester component being from 2 to 25% by weight with respect to the total amount of said extrusion-laminated resin components.

The invention is further concerned with a laminated  
30 film obtained by extrusion-laminating, onto at least one surface of a polyester film, a mixture resin comprising:

- (a) 100 parts by weight of the mixture resin component of an ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer or the mixture  
35 resin composition of said ethylene/unsaturated carboxylic

acid/(meth)acrylic acid ester copolymer with an ethylene/unsaturated carboxylic acid copolymer and/or an ethylene/(meth)acrylic acid ester copolymer, the amount of the unsaturated carboxylic acid component being from 1 to 12% by weight and the amount of the (meth)acrylic acid ester component being from 2 to 25% by weight with respect to the total amount of the extrusion-laminated resin components, and

(b) not more than 30 parts by weight of an ethylene/ $\alpha$ -olefin copolymer resin having a density of 840 to 900 kg/cm<sup>3</sup>.

The invention further relates to a method of producing the laminated film by extrusion-laminating, at a resin temperature of 280 to 340 °C, the above extrusion-laminate resin onto a polyester of which the surface has been oxidized and having a surface wet tension of not smaller than 45 dyns/cm.

(Detailed Description of the Invention)

It is desired that a polyester constituting the polyester film used in the present invention chiefly contains, as an acid component, an aromatic dicarboxylic acid and, particularly, a terephthalic acid or a 2,6-naphthalenedicarboxylic acid in an amount of not smaller than 80 mol% and, preferably, not smaller than 90 mol% from the standpoint of transparency, heat resistance, toughness and gas barrier property. As the acid component, there may be further contained other aromatic dicarboxylic acid, such as isophthalic acid, phthalic acid, as well as an alicyclic dicarboxylic acid such as 1,4-cyclohexanedicarboxylic acid or an aliphatic dicarboxylic acid such as adipic acid or sebacic acid as a copolymerizable component. There may be further added trifunctional or more functional carboxylic acids such as trimellitic acid, hemimellitic acid and pyromellitic acid as copolymerizable compounds provided their amounts are



small.

As the dihydroxyl compound component constituting the polyester, there can be exemplified an aliphatic glycol such as an ethylene glycol, a propylene glycol, a 1,4-  
5 butanediol, a 1,6-hexanediol, a neopentyl glycol, a diethylene glycol and a triethylene glycol, an alicyclic diol such as 1,4-cyclohexanediol, and an aromatic dihydroxyl compound such as bisphenol A ethylene oxide adduct. Among them, it is desired to use the one  
10 containing ethylene glycol or 1,4-butanediol in an amount of not smaller than 80 mol% and, preferably, not smaller than 90 mol%. There may be further contained trifunctional or more functional hydroxyl compound such as  
15 glycerin, trimethylolpropane or the like provided their amounts are small.

As representative polyesters, there can be exemplified polyethylene terephthalate, polyethylene-2,6-naphthalene dicarboxylate and polybutylene terephthalate.

It is further desired that the polyester has an  
20 intrinsic viscosity of from 0.5 to 1.4 dl/g and, particularly, from 0.6 to 1.0 dl/g as measured at 20 °C and at a concentration of 0.4 g/100 ml in a 47/53 (volume ratio) mixture solvent of trifluoroacetic acid/methane dichloride. It is further desired that the polyester has  
25 a melting point (temperature exhibiting a maximum endothermic peak as measured by using a differential scanning calorimeter) of not lower than 210 °C and, particularly, not lower than 220 °C.

The polyester film can be industrially produced as a  
30 single-layer film of polyester by the known T-die cast film method or as a co-extruded film of two or more polyesters or by using other resin than the polyester by the T-die cast film method of the co-extrusion type. They may not be stretched, but are monoaxially stretched or  
35 biaxially stretched to enhance the adaptability as the

base material film of the packaging material, and are available in the market. It is, however, desired to use the biaxially stretched films since they exhibit markedly improved toughness, transparency, heat resistance and gas barrier property.

In the present invention, the resin to be extrusion-laminated on the polyester film is an ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer or a mixture resin composition thereof with an ethylene/unsaturated carboxylic acid copolymer and/or an ethylene/(meth)acrylic acid ester copolymer, the amount of the unsaturated carboxylic acid component being from 1 to 12% by weight and the amount of the (meth)acrylic acid ester component being from 2 to 25% by weight with respect to the total amount of the resin components. That is, either the ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer is used alone or a mixture resin thereof with the ethylene/unsaturated carboxylic acid copolymer and/or the ethylene/(meth)acrylic acid ester copolymer is used. In either case, the unsaturated carboxylic acid component is contained in an amount of from 1 to 12% by weight and, preferably, from 2 to 6% by weight, and the (meth)acrylic acid ester component is contained in an amount of from 2 to 25% by weight and, preferably, from 6 to 20% by weight, as resins to be extrusion-laminated.

When the amount of the unsaturated carboxylic acid component is smaller than the above-mentioned range, the extrusion-laminated resin loses the polarity and poorly adheres to other polar base member such as polyester film or aluminum foil, and the utility of the laminated film is adversely affected. When the amount of the unsaturated carboxylic acid exceeds the above-mentioned range, on the other hand, the resin loses heat resistance, the unmolten products forms due to the dehydration crosslinking

reaction during the extrusion-laminate processing, and foams develop conspicuously due to water. When the amount of the (meth)acrylic acid ester component is smaller than the above-mentioned range, affinity decreases between the extrusion-laminated resin and the polyester film, and the adhesiveness to the polyester decreases. When the amount of the (meth)acrylic acid ester component exceeds the above-mentioned range, on the other hand, the stickiness increases during the extrusion-laminate processing, deteriorating the adaptability for processing.

As the unsaturated carboxylic acid in the ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer, there can be exemplified acrylic acid, methacrylic acid, ethacrylic acid, fumaric acid, maleic acid, monomethyl maleate and maleic anhydride. Among them, it is particularly desired to use a copolymer of acrylic acid or methacrylic acid. The (meth)acrylic acid ester in the copolymer stands for an acrylic acid ester or a methacrylic acid ester. Concrete examples include esters of such as methyl, ethyl, n-butyl, isobutyl, 2-ethylhexyl, and isooctyl. In the copolymer, the unsaturated carboxylic acid is contained in an amount of, desirably, from 1 to 15% by weight and, particularly, from 2 to 12% by weight, and the (meth)acrylic acid ester is contained in an amount of from 4 to 25% by weight and, particularly, from 6 to 20% by weight. It is further desired that the copolymer has a melt flow rate (MFR) of from 0.5 to 100 g/10 min. and, particularly, from 1 to 50 g/10 min. at 190 °C under a load of 2160 g.

As the ethylene/unsaturated carboxylic acid copolymer that can be used together with the ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer, there can be exemplified copolymers of ethylene with acrylic acid, methacrylic acid, ethacrylic acid, fumaric acid, maleic acid, monomethyl maleate or maleic anhydride.

Among them, it is particularly desired to use an ethylene/acrylic acid copolymer or an ethylene/methacrylic acid copolymer. It is desired that the content of the unsaturated carboxylic acid in the copolymer is from 1 to 15% by weight and, particularly, from 2 to 12% by weight. It is further desired that the copolymer has an MFR of from 0.5 to 100 g/10 min. and, particularly, from 1 to 50 g/10 min. at 190 °C under a load of 2160 g.

As the ethylene/(meth)acrylic acid ester copolymer that can be used together with the ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer, there can be exemplified a copolymer of an ethylene and a (meth)acrylic acid ester. As the ester component, there can be exemplified esters of such as methyl, ethyl, n-butyl, isobutyl, 2-ethylhexyl and isooctyl. It is further desired that the copolymer has an MFR of from 0.5 to 100 g/10 min. and, particularly, from 1 to 50 g/10 min. at 190 °C under a load of 2160 g.

These ethylene copolymers are obtained by the radical copolymerization at a high temperature and under an elevated pressure.

In the second invention, the resin to be extrusion-laminated is a mixture resin comprising:

(a) 100 parts by weight of the mixture resin component of an ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer or the mixture resin composition of said ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer with an ethylene/unsaturated carboxylic acid copolymer and/or an ethylene/(meth)acrylic acid ester copolymer, the amount of the unsaturated carboxylic acid component being from 1 to 12 % by weight and the amount of the (meth)acrylic acid ester component being from 2 to 25 % by weight with respect to the total amount of the extrusion-laminated resin components, and

(b) not more than 30 parts by weight and preferably, from 5 to 20 parts by weight, and more preferably, from 10 to 20 parts by weight, of an ethylene/ $\alpha$ -olefin copolymer resin having a density of 840 to 900 kg/m<sup>3</sup>.

5       The ethylene/ $\alpha$ -olefin copolymer is a random copolymer of an ethylene and an  $\alpha$ -olefin, such as propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene or 4-methyl-1-pentene. As such a copolymer, it is desired to use a copolymer of an ethylene and an  $\alpha$ -olefin  
10       having about 4 to about 8 carbon atoms. Further, the copolymer has a density of from 840 to 900 kg/m<sup>3</sup> and, desirably, from 860 to 890 kg/m<sup>3</sup>.

      The ethylene/ $\alpha$ -olefin copolymer is used for enhancing the adhesive force to the polyester film. When  
15       the density exceeds the above-mentioned range, however, the adhesion to the polyester film is not so much improved. When the density becomes smaller than the above range, on the other hand, the resin becomes so sticky that the handling is deteriorated during the extrusion-  
20       lamination processing. When the blended amount exceeds the above-mentioned range, further, the extrusion-laminate processability greatly decreases.

      It is further desired that the copolymer has an MFR of from 0.5 to 200 g/10 min. and, particularly, from 1 to  
25       50 g/10 min. at 190 °C under a load of 2160 g. Such a copolymer can be produced by using a combination catalyst of, for example, a transition metal catalyst component such as vanadium compound, zirconium compound or metallocene compound and an organic aluminum compound  
30       catalyst component.

      The second invention is the same as the first invention except that the amount of the unsaturated carboxylic acid component is from 1 to 12% by weight and, preferably, from 2 to 6% by weight and the amount of the  
35       (meth)acrylic acid ester component is from 2 to 25% by

weight and, preferably, from 6 to 20% by weight based on the ethylene/polar monomer copolymer in the extrusion-laminated resin.

In the first and second inventions, it is desired  
5 that the extrusion-laminated resin has been so adjusted as to exhibit an MFR of from 0.5 to 100 g/10 min. and, particularly, from 1 to 50 g/10 min. at 190 °C under a load of 2160 g by taking the extrusion-laminate processability into consideration.

10 Further, the carboxylic acid group of the unsaturated carboxylic acid in the extrusion-laminated resin may be partly ionized with an alkali metal or an alkaline earth metal within a range in which the ionization degree is not larger than 20% and, particularly, not larger than 10%.  
15 When the ionization degree exceeds 20%, the adhesive force to the polyester film decreases, which is not desirable.

If necessary, further, the resin to be extrusion-laminated may be blended with various additives, such as antioxidant, heat stabilizer, slipping agent and anti-  
20 blocking agent. Concretely speaking, as the slipping agent or the anti-blocking agent, there can be used one or two or more of amides of saturated fatty acid or unsaturated fatty acid, such as stearic acid amide, oleic acid amide, erucic acid amide, palmitic acid amide, oleyl  
25 palmitamide, stearyl erucamide, N,N'-ethylenebis erucamide, hydrogenated castor oil and silica. It is desired that they are used in an amount of from 0.1 to 5 parts by weight and, particularly, from 0.3 to 3 parts by weight per 100 parts by weight of the extrusion-lamination  
30 resin.

The laminated film according to the first invention and the second invention can be produced by using a known extrusion laminator. Described below in detail is a method of producing a laminated film of a two-layer  
35 structure comprising a biaxially stretched polyester

film/extrusion-laminated resin, which is the simplest constitution of the invention and is a representative embodiment.

The biaxially stretched polyester film is delivered  
5 at a constant speed from the base member film delivery portion and is guided to a laminating portion. In the laminating portion, a thin molten film of the to-be-laminated resin heated and melted at a predetermined temperature in the cylinder and is continuously extruded  
10 in the form of a thin film from the T-die, is permitted to be hanged directly on the surface of the biaxially stretched polyester film, and the biaxially stretched polyester film and the laminated resin are press-adhered together and cooled simultaneously between the cooling  
15 roll and the press-adhering roll, and are then taken up as a product in the take-up portion.

It is desired that the to-be-laminated surface of the biaxially stretched polyester film has a surface wet tension of not smaller than 45 dyns/cm and, more  
20 preferably, not smaller than 50 dyns/cm for producing a sufficiently large adhesive force to the extrusion-laminated resin. When the surface wet tension is smaller than 45 dyns/cm, the adhesive force is not sufficient. In order for the surface wet tension of the biaxially  
25 stretched polyester film to assume the above-mentioned level, the surface of the film may be oxidized relying upon a known industrial method such as corona treatment or flame treatment. The surface oxidation treatment may be executed in a step of producing the biaxially stretched  
30 polyester film or just before the lamination in the step of extrusion-lamination.

It is desired that the extrusion temperature during the extrusion-lamination processing is from 280 to 340 °C and, particularly, from 300 to 330 °C as the resin  
35 temperature measured just under the T-die. When the resin

temperature is lower than 280 °C, the adhesive force is not sufficient between the laminated resin and the polyester film. When the resin temperature is higher than 340 °C, on the other hand, the laminated resin is

5 thermally deteriorated to a conspicuous degree.

The two layer-laminated film comprising the polyester film and the extrusion-laminated resin exhibits excellent interlayer adhesiveness to the polyester film owing to the laminated resin, as well as excellent heat-sealing

10 property and hot-tacking property, and can be extensively used as a film for pillow packaging for packaging foods and industrial materials, and as plastic films, sheets, and as a film for thermal lamination on the sheets, papers, metals, woods, etc.

15 In the laminated film of the invention, other polar member that plays the role of reinforcement can be further laminated on the polyester film via the laminated resin. As the polar base member, there can be exemplified those members having metallic or ceramic surfaces, such as

20 aluminum foil, aluminum-deposited polyester film, aluminum-deposited polypropylene film, silica-deposited polyester film, and alumina-deposited polyester film, as well as plastic films and papers, such as polyamide, ethylene/vinyl alcohol copolymer, etc.

25 When the polar base member is to be further laminated, there can be employed the so-called extrusion sandwich-lamination method according to which the polyester film is fed from the delivering portion to the laminating portion like in the above-mentioned extrusion-

30 lamination method, the laminated resin is stacked on the polyester film and, at the same time, the polar base member film is fed even from the side opposite to the surface where the laminated resin and the polyester film are laminated one upon the other, so as to be laminated on

35 the laminated resin. According to the sandwich-lamination



method, contrary to the above-mentioned procedure, the polar base member is fed from the delivering portion to the laminating portion, the extrusion-laminated resin is stacked on the polar base member and, at the same time, the polyester film is fed from the side opposite to the surface where the laminated resin and the polar base member are laminated one upon the other, so as to be laminated on the laminated resin, which is the extrusion sandwich-lamination method.

Described below are representative examples of laminations of the polyester film and various polar base members via the extrusion-laminated resin. Here, the extrusion-laminated surface of the polar base member may, as required, be oxidized. Usually, however, the laminated resin in the present invention tends to exhibit favorable extrusion-lamination strength for the polar base member without treatment. It is therefore sufficient to install the surface oxidation treatment facility only on the side of the extrusion-laminated surface of the biaxially stretched polyester film.

- (a) O-PET/EX/aluminum foil
- (b) O-PET/EX/aluminum-deposited polyester
- (c) O-PET/EX/aluminum-deposited polypropylene
- (d) O-PET/EX/alumina-deposited polyester
- (e) O-PET/EX/ethylene-vinyl alcohol copolymer
- (f) O-PET/EX/paper

Here, O-PET stands for a biaxially stretched polyester film, and EX stands for an extrusion-laminated resin.

If necessary, further, there may be laminated any other base material film and, for this purpose, there may be employed any known method such as the extrusion laminator that is repetitively used, the tandem laminator or the dry laminator, to obtain a desired laminated film.

There is no particular limitation on the thickness of

the laminated film. Usually, however, the polyester film has a thickness of from 1 to 1000  $\mu\text{m}$  and the extrusion-laminated resin layer has a thickness of from 3 to 300  $\mu\text{m}$ .  
(EXAMPLES)

5 Described below are Examples and Comparative Examples for explaining the effect of the present invention. The starting laminated resin materials used in Examples and in Comparative Examples, method of producing laminated films, and method of evaluating the laminated films were as  
10 described below.

1. Starting resin materials to be laminated.

(A-1) Ethylene/methacrylic acid/isobutyl acrylate copolymer ①.

Content of methacrylic acid: 4% by weight, content of  
15 isobutyl acrylate: 15% by weight, MFR: 27 g/10 min.

(A-2) Ethylene/methacrylic acid/isobutyl acrylate copolymer ②.

Content of methacrylic acid: 11% by weight, content of isobutyl acrylate: 8% by weight, MFR: 10 g/10 min.

20 (B-1) Ethylene/methacrylic acid copolymer ①.

Content of methacrylic acid: 4% by weight, MFR: 7 g/10 min.

(B-2) Ethylene/acrylic acid copolymer ②.

Content of acrylic acid: 5% by weight, MFR: 8 g/10  
25 min.

(C-1) Ethylene/ $\alpha$ -olefin copolymer ①.

$\alpha$ -olefin: 1-butene, density: 885 kg/m<sup>3</sup>, MFR: 3.6 g/10 min.

(C-2) Ethylene/ $\alpha$ -olefin copolymer ②.

$\alpha$ -olefin: 1-butene, density: 860 kg/m<sup>3</sup>, MFR: 35 g/10  
30 min.

(C-3) Ethylene/ $\alpha$ -olefin copolymer ③.

$\alpha$ -olefin: 1-octene, density: 870 kg/m<sup>3</sup>, MFR: 35 g/10 min.

35 (D-1) Polyethylene ①

Density: 917 kg/m<sup>3</sup>, MFR 7.0 g/10 min.

(E-1) Ethylene/ethyl acrylate copolymer ①

Content of ethyl acrylate: 9% by weight, MFR: 5 g/10 min.

5 2. Method of producing laminated films.

2-1. Constitutions of laminated films.

Lamination constitution ①: O-PET/laminated resin (25 μm)

Lamination constitution ②: O-PET/laminated resin (25 μm)/base member film (a)

10 Lamination constitution ③: O-PET/laminated resin (25 μm)/base member film (b)

O-PET: Biaxially stretched polyester film (12 μm),  
P60 (one surface is corona-treated) produced  
by Toray Co.

15 Base member film (a): aluminum foil (7 μm)/biaxially stretched polyester film (12 μm)

Base member film (b): polyethylene (20 μm)/anchor-coating agent/biaxially stretched polyester film (12 μm).

2-2. Method of extrusion-lamination.

Resin pellets prepared to have a predetermined composition were melt-extruded onto the biaxially stretched polyester film by using an extrusion laminator, to prepare laminated films having the above-mentioned lamination constitutions ①, ② and ③ under the following production conditions.

Extrusion laminator: 65 mm-diameter extruder,  
30 opening width of T-die, 500 mm.

Extrusion laminator processing rate: 80 m/min.

Extruded resin temperature: 270 to 350 °C (resin temperature just under the T-die is measured using a contact-type thermometer).

Air gap: 120 mm

In the case of the lamination constitution ①, the biaxially stretched polyester film was delivered, and the resin to be laminated was laminated by extrusion. In the cases of the lamination constitutions ② and ③, the biaxially stretched polyester film was delivered, and the resin to be laminated was sandwich-laminated on the base member films (a) and (b), respectively.

3. Items to be evaluated and methods of evaluation.

3-1. Extrusion-lamination processability of the laminated resin.

The stability of the laminated film during the extrusion-lamination processing in 2-2 above was evaluated by naked eyes. In this observation by eyes, there were maintained the sampling conditions of laminated films at a processing rate of 80 m/min. and a thickness of extruded laminate of 25  $\mu\text{m}$ , and the extrusion conditions of a processing rate of 80 m/min. and a thickness of the extruded laminate of 25  $\mu\text{m}$ . A maximum processing rate was evaluated while gradually increasing the processing rate only. The target of extrusion-lamination processability was set to be the maximum processing rate of not smaller than 200 m/min, and the processing rates of lower than this value were judged to be of not practicable levels.

3-2. Adhesiveness between the polyester film and the laminated resin.

An extrusion-laminated sample (lamination constitution ③) two days after the production was measured under the conditions of a sample width of 15 mm, a peeling angle of 90 degrees and a tension speed of 300 mm/min. The degree of oxidation on the laminated surface of the polyester film was judged relying upon a measured value of surface wet tension. The surface wet tension was measured by using a wet tension measuring solution (produced by Wako Junyaku Co.). A target value of the

adhesion strength was set to be 3 N/15 mm, and the adhesion strengths smaller than this value were judged to be of not practicable levels.

3-3. Adhesiveness between the aluminum foil and the  
5 laminated resin.

An extrusion-laminated sample (lamination constitution ②) one day after the production was measured under the conditions of a sample width of 15 mm, a peeling angle of 90 degrees and a tension speed of 300 mm/min. A  
10 target value of the adhesion strength was set to be 2 N/15 mm, and the adhesion strengths smaller than this value were judged to be of not practicable levels.

3-4. Heat-sealing property of the laminated film.

The laminated resin surfaces of the samples  
15 (lamination constitution ①) were heat-sealed by using a heat sealer to measure the heat-sealing strength. The heat sealer was a one surface-heated bar sealer (produced by Toyo Seiki co.), and the sealing pressure was 0.2 MPa (real pressure) and the sealing time was 0.5 seconds. A  
20 maximum target strength of the heat sealing was set to be not smaller than 30 N/15 mm, and strengths smaller than this value were judged to be of not practicable levels.  
(Example 1)

By using a resin composition of (A-1)  
25 ethylene/methacrylic acid/isobutyl acrylate copolymer ① and (B-1) ethylene/methacrylic acid copolymer ① blended at a ratio shown in Table 1 as a resin to be extrusion-laminated, there were prepared the lamination constitutions ①, ② and ③ by the method of producing the  
30 laminated film described in 2. above, and were evaluated for their extrusion-lamination processability, adhesive force to the polyester film, adhesive force to the aluminum foil and heat-sealing strength according to the items to be evaluated and methods of evaluation described  
35 in 3. above.

In conducting the extrusion-lamination processing, the resin temperature was set to 300 °C, and the above resin composition was extrusion-laminated on the surface of the polyester film of the side corona-treated. The results were as shown in Table 1.  
(Example 2)

The laminated film was prepared according to the same method and under the same conditions as those of Example 1 but changing the resin temperature during the extrusion-lamination processing to 320 °C, and the extrusion-lamination processability and the physical properties were evaluated. The results were as shown in Table 1.  
(Comparative Example 1)

The laminated film was prepared according to the same method and under the same conditions as those of Example 1 but changing the resin temperature during the extrusion-lamination processing to 270 °C, and was evaluated. The obtained laminated film exhibited an adhesive force to the polyester film of as very low as 0.1 N/15 mm. The heat-sealing strength did not reach the practicable level, and the laminated film was judged to be not suited as a packaging material. The results were as shown in Table 1.  
(Comparative Example 2)

The extrusion-lamination processing was conducted according to the same method and under the same conditions as those of Example 1 but changing the resin temperature during the extrusion-lamination processing to 350 °C. In this case, however, the resin composition developed foaming during the extrusion-lamination processing, and the laminated film of the molten state was perforated. Therefore, the laminated film could not be sampled and could not be evaluated. The results were as shown in Table 1.

(Comparative Example 3)

The laminated film was prepared according to the same

method and under the same conditions as those of Example 1 but laminating the polyester film on the surface of the side not treated with corona (surface wet tension of 44 dyns/cm) and changing the resin temperature to 320 °C, and  
5 its physical properties were evaluated. The obtained laminated film exhibited an adhesive force to the polyester film of as very low as 0.8 N/15 mm. The heat-sealing strength did not reach the practicable level, and the laminated film was judged to be not suited as a  
10 packaging material. The results were as shown in Table 1. (Example 3)

A laminated film was prepared according to the same method and under the same conditions as those of Example 1 but using (A-2) ethylene/methacrylic acid, isobutyl  
15 acrylate copolymer ② alone as the resin to be extrusion-laminated, and its physical properties were evaluated. The results were as shown in Table 1. (Example 4)

By using a resin composition of (A-2)  
20 ethylene/methacrylic acid/isobutyl acrylate copolymer ② and (C-1) ethylene/ $\alpha$ -olefin copolymer ① blended at a ratio shown in Table 1 as a resin to be extrusion-laminated, there were prepared the lamination  
constitutions ①, ② and ③ by the method of producing the  
25 laminated film described in 2. above, and were evaluated for their extrusion-lamination processability, adhesive force to the polyester film, adhesive force to the aluminum foil and heat-sealing strength according to the items to be evaluated and methods of evaluation described  
30 in 3. above.

In conducting the extrusion-lamination processing, the resin temperature was set to 285 °C, and the above resin composition was extrusion-laminated on the surface of the polyester film of the side corona-treated. The  
35 results were as shown in Table 2.

## (Example 5)

A laminated film was prepared according to the same method and under the same conditions as those of Example 4 but using (C-2) ethylene/ $\alpha$ -olefin copolymer ② instead of the component (C-1) as the resin to be extrusion-laminated and changing the resin temperature during the extrusion-lamination processing to 300 °C, and was evaluated. The results were as shown in Table 2.

## (Example 6)

A laminated film was prepared according to the same method and under the same conditions as those of Example 4 but using (C-3) ethylene/ $\alpha$ -olefin copolymer ③ instead of the component (C-1) as the resin to be extrusion-laminated and changing the resin temperature during the extrusion-laminate processing to 300 °C, and was evaluated. The results were as shown in Table 2.

## (Comparative Example 4)

The laminated film was prepared according to the same method and under the same conditions as those of Example 5 but laminating the polyester film on the surface of the side not treated with corona (surface wet tension of 44 dyns/cm), and was evaluated. The obtained laminated film exhibited an adhesive force to the polyester film of as very low as 0.7 N/15 mm. The heat-sealing strength did not reach the practicable level, and the laminated film was judged to be not suited as a packaging material. The results were as shown in Table 2.

## (Example 7)

Properties were evaluated by according to the same method and under the same conditions as those of Example 1 but using a resin composition of (A-1) ethylene/methacrylic acid/isobutyl acrylate copolymer ①, (B-1) ethylene/methacrylic acid copolymer ① and (C-1) ethylene/ $\alpha$ -olefin copolymer ① blended at a ratio shown in Table 2 as a resin to be extrusion-laminated and



changing the resin temperature to 315 °C. The results were as shown in Table 2.

(Comparative Example 5)

The laminated film was prepared according to the same method and under the same conditions as those of Example 7 but laminating the polyester film on the surface of the side not treated with corona (surface wet tension of 44 dyns/cm), and was evaluated. The obtained laminated film exhibited an adhesive force to the polyester film of as very low as 0.6 N/15 mm. The heat-sealing strength did not reach the practicable level, and the laminated film was judged to be not suited as a packaging material. The results were as shown in Table 2.

(Example 8)

Properties were evaluated according to the same method and under the same conditions as those of Example 1 but using a resin composition of (A-2) ethylene/methacrylic acid/isobutyl acrylate copolymer ② and (C-2) ethylene/ $\alpha$ -olefin copolymer ② blended at a ratio shown in Table 3 as a resin to be extrusion-laminated, delivering the surface of the polyester film which has not been treated with corona as the surface to be laminated, and executing the extrusion-lamination by effecting the corona-treatment using a corona-treating apparatus installed in the laminator just prior to executing the extrusion-lamination. The corona-treating conditions were as follows:

Corona-treating apparatus: Manufactured by Kasuga  
Denki Co.

Treating condition: 40 W/m<sup>2</sup>/min.  
Surface wet tension after the treatment: 58 dyns/cm  
The results were as shown in Table 3.

(Example 9)

The laminated film was prepared according to the same method and under the same conditions as those of Example 1

but so preparing the resin composition of Example 1 that 18% of the carboxylic acid group of the unsaturated carboxylic acid was ionized with zinc and changing the temperature of the extrusion-laminated resin to 315 °C, and its physical properties were evaluated. The results were as shown in Table 4.  
(Comparative Example 6)

The extrusion-lamination processing was executed according to the same method and under the same conditions as those of Example 1 but using a resin composition of (A-2) ethylene/methacrylic acid/isobutyl acrylate copolymer ② and (C-1) ethylene/ $\alpha$ -olefin copolymer ① blended at a ratio shown in Table 3 as a resin to be extrusion-laminated and changing the resin temperature to 315 °C. In this case, however, both ends of the molten resin film swung to a large extent during the extrusion-lamination processing and did not remain stable. Therefore, the laminated layer coupled not be sampled. The results were as shown in Table 3.

(Comparative Example 7)

The laminated film was prepared according to the same method and under the same conditions as those of Example 1 but using (B-2) ethylene/acrylic acid copolymer ② alone as a resin to be extrusion-laminated and changing the resin temperature to 310 °C. The obtained laminated film exhibited an adhesive force to the polyester film of as very low as 0.6 N/15 mm. The heat-sealing strength did not reach the practicable level, and the laminated film was judged to be not suited as a packaging material. The results were as shown in Table 3.

(Comparative Example 8)

Properties were evaluated according to the same method and under the same conditions as those of Example 1 but using a resin composition of (B-2) ethylene/acrylic acid copolymer ② and (C-2) ethylene/ $\alpha$ -olefin copolymer

② blended at a ratio shown in Table 3 as a resin to be extrusion-laminated and changing the resin temperature to 310 °C. The obtained laminated film exhibited an adhesive force to the polyester film of as low as 1.7 N/15 mm. The heat-sealing strength did not reach the practicable level, and the laminated film was judged to be not suited as a packaging material. The results were as shown in Table 3. (Comparative Example 9)

Properties were evaluated according to the same method and under the same conditions as those of Example 1 but using (D-1) polyethylene alone as a resin to be extrusion-laminated. The obtained laminated film exhibited an adhesive force to the polyester film of 2.6 N/15 mm which was slightly smaller than the target strength. The adhesive strength to the aluminum foil did not reach the practicable level, and the laminated film was judged to be not suited as a packaging material. (Comparative Example 10)

Properties were evaluated according to the same method and under the same conditions as those of Example 1 but using (E-1) ethylene/ethyl acrylate copolymer ① alone as a resin to be extrusion-laminated. The obtained laminated film exhibited an adhesive force to the polyester film of as very small as 0.9 N/15 mm. Besides, the adhesive strength to the aluminum foil was very small, and the laminated film was judged to be not suited as a packaging material. (Comparative Example 11)

The laminated film was prepared according to the same method and under the same conditions as those of Example 1 but so preparing the resin composition of Example 1 that 35% of the carboxylic acid based on the unsaturated carboxylic acid was ionized with zinc and changing the temperature of the extrusion-laminated resin to 315 °C, and its physical properties were evaluated. The results

were as shown in Table 4.

As will be obvious from Tables 1 to 3, it was confirmed that a laminate having a practically sufficient adhesive force to the polyester and heat-sealing property was obtained by extrusion-laminating the resin composition of the present invention onto a polyester film according to a predetermined extrusion-lamination processing method and under predetermined conditions. It was further confirmed that the resin composition of the invention exhibited excellent extrusion-lamination adhesiveness to the polar base member as represented by an aluminum foil, and was suited for laminating the polyester film with various polar base members.

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Table 1

| Laminated-resin composition<br>(pts by wt.)                         |  | Example<br>1 | Example<br>2 | Comparative<br>Example 1 | Comparative<br>Example 2 | Comparative<br>Example 3 | Example<br>3 |
|---|--|--------------|--------------|--------------------------|--------------------------|--------------------------|--------------|
| (A-1) Copolymer ①   |  | 50           | 50           | 50                       | 50                       | 50                       | 100          |
| (A-2) Copolymer ②   |  |              |              |                          |                          |                          |              |
| (B-1) Ethylene/methacrylic<br>acid copolymer ①                      |  | 50           | 50           | 50                       | 50                       | 50                       |              |
| (B-2) Ethylene/acrylic acid<br>copolymer ②                          |  |              |              |                          |                          |                          |              |
| (C-1) Ethylene/ $\alpha$ -olefin<br>copolymer ①                     |  |              |              |                          |                          |                          |              |
| (C-2) Ethylene/ $\alpha$ -olefin<br>copolymer ②                     |  |              |              |                          |                          |                          |              |
| (C-3) Ethylene/ $\alpha$ -olefin<br>copolymer ③                     |  |              |              |                          |                          |                          |              |
| (D-1) Polyethylene  |  |              |              |                          |                          |                          |              |
| (E-1) Ethylene/ethyl acrylate<br>copolymer                          |  |              |              |                          |                          |                          |              |
| Content of copolymer component<br>in the laminated resin (% by wt.) |  |              |              |                          |                          |                          |              |
| Unsaturated carboxylic acid   |  | 4            | 4            | 4                        | 4                        | 4                        | 11           |
| (meth)acrylic acid ester  |  | 7.5          | 7.5          | 7.5                      | 7.5                      | 7.5                      | 8            |

Table 1 (continued)

|   | Example<br>1 | Example<br>2 | Comparative<br>Example 1 | Comparative<br>Example 2  | Comparative<br>Example 3 | Example<br>3 |
|---|--------------|--------------|--------------------------|---------------------------|--------------------------|--------------|
| <u>Extrusion-laminated resin temp. (°C)</u>                                     | 300          | 320          | 270                      | 350                       | 320                      | 300          |
| <u>Surface wet tension of laminated<br/>surface of polyester film (dyns/cm)</u> | 56           | 56           | 56                       | 56                        | 44                       | 56           |
| <u>Extrusion-lamination processability</u>                                      |              |              |                          |                           |                          |              |
| Max. Processing rate (m/min)  | 400<         | 400<         | 300                      |                           | 400<                     | 400<         |
| Condition of laminated film   | ○            | ○            | ○                        | ×                         | ○                        | ○            |
| <u>Adhesive force to polyester film<br/>(N/15 mm)</u>                           | 6.9          | 10.6         | 0.1<                     | could not<br>be evaluated | 0.8                      | 4.6          |
| <u>Adhesive force to aluminum foil<br/>(N/15 mm)</u>                            | 2.7          | 2.8          | 2.8                      | could not<br>be evaluated | 2.8                      | 2.8          |
| <u>Heat-sealing strength (N/15 mm)</u>  |              |              |                          |                           |                          |              |
| 120 °C  | 35           | 37           | 12                       | could not<br>be evaluated | 14                       | 39           |
| 140 °C  | 36           | 38           | 14                       | could not<br>be evaluated | 16                       | 40           |
| 160 °C  | 36           | 38           | 13                       | could not<br>be evaluated | 16                       | 41           |

Table 2

| Laminated-resin composition<br>(pts by wt.)                      | Example 4 |           |                       |           |           |
|--|-----------|-----------|-----------------------|-----------|-----------|
|  | Example 4 | Example 5 | Comparative Example 4 | Example 6 | Example 7 |
| (A-1) Copolymer ①  |           |           |                       |           | 45        |
| (A-2) Copolymer ②  |           |           |                       |           | 45        |
| (B-1) Ethylene/methacrylic acid copolymer ①                      | 90        | 90        | 90                    | 90        |           |
| (B-2) Ethylene/acrylic acid copolymer ②                          |           |           |                       |           | 45        |
| (C-1) Ethylene/ $\alpha$ -olefin copolymer ①                     | 10        |           |                       |           | 10        |
| (C-2) Ethylene/ $\alpha$ -olefin copolymer ②                     |           | 10        | 10                    |           |           |
| (C-3) Ethylene/ $\alpha$ -olefin copolymer ③                     |           |           |                       | 10        |           |
| (D-1) Polyethylene   |           |           |                       |           |           |
| (E-1) Ethylene/ethyl acrylate copolymer                          |           |           |                       |           |           |
| Content of copolymer component in the laminated resin (% by wt.) |           |           |                       |           |           |
| Unsaturated carboxylic acid                                      | 9.9       | 9.9       | 9.9                   | 9.9       | 3.6       |
| (meth)acrylic acid ester   | 7.2       | 7.2       | 7.2                   | 7.2       | 6.8       |

Table 2 (continued)

|   | Example<br>4 | Example<br>5  | Comparative<br>Example 4 | Example<br>6  | Example<br>7  | Comparative<br>Example 5 |
|---|--------------|---------------|--------------------------|---------------|---------------|--------------------------|
| <u>Extrusion-laminated resin temp. (°C)</u>                                 | 285          | 300           | 300                      | 300           | 315           | 315                      |
| <u>Surface wet tension of laminated surface of polyester film (dyns/cm)</u> | 56           | 56            | 44                       | 56            | 56            | 44                       |
| <u>Extrusion-lamination processability</u>                                  |              |               |                          |               |               |                          |
| Max. Processing rate (m/min)  | 400<         | 400<          | 400<                     | 370           | 400<          | 400<                     |
| Condition of laminated film   | ○            | ○             | ○                        | ○             | ○             | ○                        |
| <u>Adhesive force to polyester film (N/15 mm)</u>                           | 3.5          | 7.1           | 0.7                      | 5.4           | 9.4           | 0.6                      |
| <u>Adhesive force to aluminum foil (N/15 mm)</u>                            | 2.6          | 2.8           | 2.8                      | 2.8           | 2.8           | 2.8                      |
| <u>Heat-sealing strength (N/15 mm)</u>                                      |              |               |                          |               |               |                          |
| 120 °C  | 37           | not evaluated | 15                       | not evaluated | not evaluated | not evaluated            |
| 140 °C  | 39           | not evaluated | 17                       | not evaluated | not evaluated | not evaluated            |
| 160 °C  | 39           | not evaluated | 16                       | not evaluated | not evaluated | not evaluated            |



Table 3

| Laminated-resin composition<br>(pts by wt.)                         |  | Example<br>8 | Comparative<br>Example 6 | Comparative<br>Example 7 | Comparative<br>Example 8 | Comparative<br>Example 9 | Comparative<br>Example 10 |
|---|--|--------------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------------|
| (A-1) Copolymer ①   |  | 90           | 65                       |                          |                          |                          |                           |
| (A-2) Copolymer ②   |  |              |                          |                          |                          |                          |                           |
| (B-1) Ethylene/methacrylic<br>acid copolymer ①                      |  |              |                          |                          |                          |                          |                           |
| (B-2) Ethylene/acrylic acid<br>copolymer ②                          |  |              | 100                      |                          | 90                       |                          |                           |
| (C-1) Ethylene/ $\alpha$ -olefin<br>copolymer ①                     |  |              | 35                       |                          |                          |                          |                           |
| (C-2) Ethylene/ $\alpha$ -olefin<br>copolymer ②                     |  | 10           |                          |                          | 10                       |                          |                           |
| (C-3) Ethylene/ $\alpha$ -olefin<br>copolymer ③                     |  |              |                          |                          |                          | 100                      |                           |
| (D-1) Polyethylene  |  |              |                          |                          |                          |                          | 100                       |
| (E-1) Ethylene/ethyl acrylate<br>copolymer                          |  |              |                          |                          |                          |                          |                           |
| Content of copolymer component<br>in the laminated resin (% by wt.) |  |              |                          |                          |                          |                          |                           |
| Unsaturated carboxylic acid   |  | 9.9          | 7.2                      | 5                        | 4.5                      | 0                        | 0                         |
| (meth)acrylic acid ester  |  | 7.2          | 5.2                      | 0                        | 0                        | 0                        | 9                         |

Table 3 (continued)

|   |  | Example 8     | Example 6              | Example 7 | Example 8 | Example 9     | Comparative Example 10 |
|---|--|---------------|------------------------|-----------|-----------|---------------|------------------------|
| <u>Extrusion-laminated resin temp. (°C)</u>                                 |  | 300           | 315                    | 310       | 310       | 300           | 300                    |
| <u>Surface wet tension of laminated surface of polyester film (dyns/cm)</u> |  | 58            | 56                     | 56        | 56        | 56            | 56                     |
| <u>Extrusion-lamination processability</u>                                  |  |               |                        |           |           |               |                        |
| Max. Processing rate (m/min)  |  | 370           |                        | 400<      | 350       | 200           | 220                    |
| Condition of laminated film   |  | ○             | ×                      | ○         | ○         | ○             | ○                      |
| Adhesive force to polyester film (N/15 mm)                                  |  | 7.9           | could not evaluated    | 0.6       | 1.7       | 2.6           | 0.9                    |
| Adhesive force to aluminum foil (N/15 mm)                                   |  | not evaluated | could not evaluated    | 3.7       | 3.5       | 1.6           | 0.3                    |
| Heat-sealing strength (N/15 mm)   |  |               |                        |           |           |               |                        |
| 120 °C  |  | not evaluated | could not be evaluated | 18        | 18        | not evaluated | not evaluated          |
| 140 °C  |  | not evaluated | could not be evaluated | 20        | 19        | not evaluated | not evaluated          |
| 160 °C  |  | not evaluated | could not be evaluated | 19        | 17        | not evaluated | not evaluated          |

Table 4

| <u>Laminated-resin composition (pts by wt.)</u>                             | <u>Example 9</u> | <u>Comparative Example 11</u> |
|---|------------------|-------------------------------|
| (A-1) Copolymer ①   | 50               | 50                            |
| (B-1) Ethylene/methacrylic acid copolymer ①                                 | 50               | 50                            |
| <u>Content of copolymer component in the laminated resin (% by wt.)</u>     |                  |                               |
| Unsaturated carboxylic acid   | 4                | 4                             |
| (meth)acrylic acid ester  | 7.5              | 7.5                           |
| <u>Ratio of ionized unsaturated carboxylic acid (%)</u>                     | 18               | 35                            |
| <u>Extrusion-laminated resin temp. (°C)</u>                                 | 315              | 315                           |
| <u>Surface wet tension of laminated surface of polyester film (dyns/cm)</u> | 56               | 56                            |
| <u>Extrusion-lamination processability</u>                                  |                  |                               |
| Max. Processing rate (m/min)  | 400<             | 400<                          |
| Condition of laminated film   | ○                | ○                             |
| <u>Adhesive force to polyester film (N/15 mm)</u>                           | 6.8              | 2.8                           |
| <u>Adhesive force to aluminum foil (N/15 mm)</u>                            | 2.6              | 2.4                           |
| <u>Heat-sealing strength (N/15 mm)</u>                                      |                  |                               |
| 120 °C  | 33               | 20                            |
| 140 °C  | 34               | 22                            |
| 160 °C  | 35               | 23                            |

According to the present invention, it is allowed to obtain a laminated film having excellent extrusion processability and exhibiting a large interlayer adhesive force upon being extrusion-laminated directly on the polyester film. Even when sandwich-laminated together with a polar base member, the laminated film exhibits good interlayer adhesive force to the polar base member. Besides, there is no need of executing the anchor-coat processing for the polyester film offering advantage from the standpoint of maintaining sanitary environment. Moreover, since the molten resin film of the extrusion-laminated resin needs not be treated with ozone, the packaging material can be produced at a low cost, offering a great merit for the manufacturers of the packaging materials. The thus obtained laminated film can be extensively used as a variety of packaging members for packaging foods such as cakes, daily dishes, beverages, processed meat, etc. which are packaged by using polyester films.

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## CLAIMS

1. A laminated film obtained by extrusion-laminating, onto at least one surface of a polyester film,  
5 an ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer or a mixture resin composition thereof with an ethylene/unsaturated carboxylic acid copolymer and/or an ethylene/(meth)acrylic acid ester copolymer, the amount of the unsaturated carboxylic acid component being  
10 from 1 to 12% by weight and the amount of the (meth)acrylic acid ester component being from 2 to 25% by weight with respect to the total amount of said extrusion-laminated resin components.

2. A laminated film obtained by extrusion-laminating, onto at least one surface of a polyester film,  
15 a mixture resin comprising:

(a) 100 parts by weight of the mixture resin component of an ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer or the mixture  
20 resin composition of said ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer with an ethylene/unsaturated carboxylic acid copolymer and/or an ethylene/(meth)acrylic acid ester copolymer, the amount of the unsaturated carboxylic acid component being from 1 to  
25 12% by weight and the amount of the (meth)acrylic acid ester component being from 2 to 25% by weight with respect to the total amount of the extrusion-laminated resin components, and

(b) not more than 30 parts by weight of an ethylene/  
30  $\alpha$ -olefin copolymer resin having a density of 840 to 900 kg/m<sup>3</sup>.

3. A laminated film according to claim 1, wherein the carboxylic acid group of the unsaturated carboxylic acid in said mixture resin composition is partly ionized  
35 with an alkali metal or an alkaline earth metal within a

range in which the ionization degree is not larger than 20%.

4. A laminated film according to claim 2, wherein the carboxylic acid group of the unsaturated carboxylic acid in said mixture resin is partly ionized with an alkali metal or an alkaline earth metal within a range in which the ionization degree is not larger than 20%.

5. A laminated film according to claim 1 or 2, wherein another polar base member is laminated on the polyester film via the extrusion-laminated resin.

6. A method of producing a laminated film by extrusion-laminating, on the surface of a polyester film of which the surface is oxidized and has a surface wet tension of not smaller than 45 dyns/cm, (1) an extrusion-lamination resin: an ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer or a mixture resin composition thereof with an ethylene/unsaturated carboxylic acid copolymer and/or an ethylene/(meth)acrylic acid ester copolymer, the amount of the unsaturated carboxylic acid component being from 1 to 12% by weight and the amount of the (meth)acrylic acid ester component being from 2 to 25% by weight with respect to the total amount of said extrusion-laminated resin components, or an ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer, or (2) an extrusion-lamination resin: a mixture resin comprising:

(a) 100 parts by weight of the mixture resin component of an ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer or the mixture resin composition of said ethylene/unsaturated carboxylic acid/(meth)acrylic acid ester copolymer with an ethylene/unsaturated carboxylic acid copolymer and/or an ethylene/(meth)acrylic acid ester copolymer, the amount of the unsaturated carboxylic acid component being from 1 to 12% by weight and the amount of the (meth)acrylic acid

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ester component being from 2 to 25% by weight with respect to the total amount of the extrusion-laminated resin components, and

(b) not more than 30 parts by weight of an ethylene/  
5  $\alpha$ -olefin copolymer resin having a density of 840 to 900 kg/m<sup>3</sup>, at a resin temperature of from 280 to 340 °C.

7. A method of producing a laminated film according to claim 6, wherein said extrusion-lamination resin is  
10 extrusion sandwich-laminated between said polyester film and another polar base member.

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 00/03904

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B27/32 C08L23/08 C09D123/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B C08L C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|---|-----------------------|
| A          | GB 1 307 843 A (ICI LTD)<br>21 February 1973 (1973-02-21)<br>page 2, line 8 - line 17<br>page 1, line 10 - line 16  | 1,2,6                 |
| A          | DATABASE WPI<br>Section Ch, Week 199518<br>Derwent Publications Ltd., London, GB;<br>Class A17, AN 1995-136526<br>XP002146713<br>& JP 07 060914 A (FUJIMORI IND CO LTD),<br>7 March 1995 (1995-03-07)<br>abstract | 1,2,6                 |
| A          | US 4 101 701 A (GORDON MICHAEL E)<br>18 July 1978 (1978-07-18)<br>claims  | 1,2,6                 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

6 September 2000

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 00/03904

| Patent document<br>cited in-search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|---|---------------------|----------------------------|---------------------|
| GB 1307843 A                              | 21-02-1973          | NONE                       |                     |
| JP 7060914 A                              | 07-03-1995          | NONE                       |                     |
| US 4101701 A                              | 18-07-1978          | NONE                       |                     |